effect on the intrinsic viscosity. The attraction term should be due to short-range van der Waals and dipole interactions of the polymer molecules with one another (relative to those between polymer and solvent). Since the changes in the solvent and polymer over the range investigated are relatively small as far as their effect on these non-ionic forces is concerned, the constancy of this term is not unreasonable. However, further experimental work, especially studies of the effect of temperature on the parameters in equation (8), is needed to confirm the validity of this interpretation.

Observations on the Rare Earths. LXII.[1] Some Observations on Solutions of Certain Rare Earth Metal Salts in Basic Solvents

BY THERALD MOELLER AND PAUL A. ZIMMERMAN

In investigations preliminary to the study of the electrolysis of rare earth metal salts in anhydrous basic solvents, it was found that certain of these anhydrous salts are moderately soluble in both ethylenediamine and monoethanolamine but only slightly soluble in morpholine. General solubility decreases were found in the order acetates, nitrates, iodides, bromides. Monoethanolamine was found by conductance studies to be superior to ethylenediamine as an ionizing solvent for weak electrolytes, but for stronger electrolytes, particularly in dilute solution, ethylenediamine was found to be superior. Morpholine was shown to be a poor electrolytic solvent for all compounds studied. In general, rare earth metal acetates were found to be weak electrolytes, whereas nitrates, bromides and iodides were fairly strong electrolytes.

Introduction

The electrodeposition of the rare earth metals is successfully effected by use of fused salts, e.g., chloride mixtures, but the possibilities of lower temperature depositions from electrolytic solutions are intriguing. Inasmuch as electrolytic deposition from aqueous solution is precluded by preferential hydrogen discharge, except possibly when mercury cathodes are employed, such procedures must of necessity involve non-aqueous systems. Reported studies on such non-aqueous systems have been singularly unproductive, except for the preparation of amalgams.

Thus, comprehensive investigations carried out a number of years ago in this Laboratory gave negative results for a variety of solvents with all cathodes except mercury.[2,3] With mercury cathodes, contrary to the earlier observations of Kettembeil,[4] amalgams were obtained upon electrolyses of solutions of the anhydrous chlorides in absolute ethanol.[3,5-7] These were then decomposed thermally to the metals. Deposition of thorium and lanthanum as carbonaceous complexes from a variety of alcohols and pyridine has been reported,[8] as has both the deposition of comparable cerium compounds from certain alcohols and the deposition of elemental cerium from isoamyl alcohol.[9] These reports lack confirmation. Other scattered literature reports are equally negative.

The highly electropositive natures of the rare earth metals and the consequent difficulty of complete reduction of their derived cations suggest that if the metals are to be electrodeposited at all, the greatest success should be achieved using highly basic solvents. Such solvents, because of their strong donor characters, provide media in which solvated electrons can readily exist and in which lower oxidation states are strongly stabilized. This is particularly well exemplified by liquid ammonia, where the stabilities of active metals such as sodium, potassium, barium, etc., have been long recognized, and it should be noted among a variety of amines.

It seems reasonable, therefore, that given a strongly basic solvent of suitably high dielectric constant and sufficiently low viscosity in which ionic rare earth metal compounds dissolve without excessive solvolysis, one might successfully electrodeposit these metals. Although ammonia seems a logical choice, its reactivity with anhydrous rare earth metal compounds to give solvolysis products of limited solubilities[3] precludes its use. Certain of the amines offer possibilities. Of the amines, ethylenediamine was suggested by Putnam and Kobe[10] as combining best the properties desired of a good solvent for a variety of inorganic salts, but it also functioned as a medium from which active metals such as sodium[10,11] could be deposited. It is of interest also that anhydrous monoethanolamine also has been reported as an electrolytic solvent from which metals such as magnesium and aluminum could be deposited.[12]

(1) For the preceding communication in this series, see T. Moeller and N. Fogel, THIS JOURNAL, 73, 4481 (1951).

(2) L. F. Audrieth and H. W. Nelson, Chem. Revs., 8, 335 (1931).

(3) B. S. Hopkins and L. F. Audrieth, Trans. Electrochem. Soc., 66, 135 (1934).

(4) W. Kettembeil, Z. anorg. Chem., 38, 213 (1904).

(5) L. F. Audrieth, E. E. Jukkola and R. E. Meints with B. S. Hopkins, THIS JOURNAL, 53, 1805 (1931).

(6) R. E. Meints, B. S. Hopkins and L. F. Audrieth, Z. anorg. allgem. Chem., 211, 238 (1933).

(7) E. E. Jukkola with L. F. Audrieth and B. S. Hopkins, THIS JOURNAL, 56, 303 (1934).

(8) I. A. Ananasiu and M. Babor, Bul. chim. Soc. Romani chim., 38, 83 (1935-36).

(9) I. A. Ananasiu and M. Babor, ibid., 37, 67 (1934).

(10) G. L. Putnam and K. A. Kobe, Trans. Electrochem. Soc., 74, 609 (1938).

(11) N. P. Fedot'ev and R. N. Kinkul'skaya, "Proc. 1st All-Union (U.S.S.R) Conf. Non-Aqueous Solns.," 1935, 114.

(12) T. P. Dirske and H. T. Briscoe, Metal Ind., 36, 284 (1938).

Studies were instituted, therefore, upon the electrolytic behaviors of certain rare earth salts in anhydrous ethylenediamine and ethanolamine, some of the more pertinent physical constants of which compounds are summarized in Table I. For comparison, the closely related substance morpholine

TABLE I

PHYSICAL CONSTANTS OF SOLVENTS EMPLOYED

Compound	B.p., °C.	Density, g./ml.	Ionization constant	Dielectric constant	Viscosity, milli-poises
Ethylenediamine	116.2	0.891[a]	8.5×10^{-5}	16.0	15.4[a]
Monoethanolamine	171.1	1.0117[a]	2.77×10^{-5}	37.72	193.46[a]
Morpholine	128.9	0.9994[b]	2.44×10^{-7}	7.33	22.3[b]

[a] Temp., 25°.   [b] Temp., 20°.

was also included. The present paper reports data on solubilities and conductances. In a subsequent communication, results of electrolysis experiments will be described.

Experimental

Materials.—The organic solvents were obtained from the Carbide and Carbon Chemicals Corporation. Ethylenediamine was purified and dehydrated by the procedure of Putnam and Kobe.[10] The anhydrous product had a specific resistance at 30° of 2.65×10^5 ohms/cm., as compared with a value of 1.52×10^5 ohms/cm. previously reported. Monoethanolamine was purified by the procedure of Dirkse and Briscoe.[12] The product boiled at 168° (uncor.), had a density of 1.0108 g./ml. at 26.5° (lit. 1.0106 g./ml.), and had a specific conductance of 1.93×10^{-5} mho/cm. at 20°. Morpholine was purified by a modification of the procedure of Dermer and Dermer.[13] The purified product had a density of 0.9863 g./ml. at 27° and a specific conductance of 3.368×10^{-8} mho/cm. These anhydrous solvents were stored under dry nitrogen in glass-stoppered flasks sealed with a wax made by melting together equal weights of rosin and beeswax. The flasks were kept in desiccators containing soda lime, magnesium perchlorate, and phosphorus(V) oxide.

Lanthanum (LA-40), neodymium (ND-28) and yttrium (YT-20) oxides were obtained from University of Illinois stocks. They were free from all but trace quantities of the other rare earth metals. These oxides were converted into anhydrous salts by high temperature reactions with excess quantities of appropriate ammonium salts,[5,14-17] followed by removal of the unreacted ammonium salts by heating first in currents of dry nitrogen and then in vacuo. Anhydrous lanthanum nitrate, neodymium bromide, neodymium iodide, neodymium acetate, yttrium iodide and yttrium acetate were so prepared. The iodide samples were somewhat basic in character. The compositions of all materials were established by analyses.

Manipulation.—All anhydrous substances were handled in a dry box through which was passed a current of commercial nitrogen which had been dried and freed from carbon dioxide by passage through concentrated sulfuric acid, soda lime and Drierite. All solutions were prepared in the dry box, and all apparatus containing such solutions was sealed before being removed.

Solubility Determinations.—Mixtures of various anhydrous rare earth compounds and the anhydrous solvents were sealed in 25 × 200 mm. test-tubes. These tubes were thermostated for one week at 30 ± 0.05° with frequent agitation. The densities of the supernatant liquids were then determined pycnometrically, and their rare earth contents were determined by precipitating the hydrous hydroxides

(13) V. H. Dermer and O. C. Dermer, THIS JOURNAL, **59**, 1148 (1937).

(14) J. B. Reed, Doctoral Dissertation, University of Illinois (1934).

(15) J. B. Reed with B. S. Hopkins and L. F. Audrieth, THIS JOURNAL, **57**, 1159 (1935).

(16) W. A. Taebel and B. S. Hopkins, Z. anorg. allgem. Chem., **235**, 62 (1937).

(17) J. B. Reed, B. S. Hopkins and L. F. Audrieth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 28.

from measured volumes by adding excess water and weighing as the ignited oxides.

Conductance Measurements.—Conductances of various solutions were determined with the A.C. bridge of an Industrial Instruments Conductivity Bridge, Type RC-8. Two conductance cells, both fitted with ground glass stoppers and employing bright platinum electrodes, were used. These had cell constants of 0.2307 cm.$^{-1}$ and 1.041 cm.$^{-1}$. Most measurements were made after solutions had been thermostated to 30 ± 0.05°. A few were made at other temperatures.

Results and Discussion

Solubility Determinations.—Solubility data obtained are summarized in Table II. It is apparent that, with the exception of the acetates, the compounds studied are only moderately soluble, an observation which is in accord with the work of Isbin and Kobe,[18] which showed that alkali metal salts are much less soluble in ethylenediamine and monoethanolamine than in water. In general, this reduction in solvent power parallels decrease in dielectric constant, all of these solvents having much lower dielectric constants than water, and morpholine, the poorest of the solvents, having the smallest dielectric constant. The enhanced solubilities of the anhydrous acetates is doubtless a reflection of their enhanced covalent natures.

TABLE II

SOLUBILITIES OF RARE EARTH METAL SALTS IN BASIC SOLVENTS AT 30°

Salt	Ethylenediamine	Monoethanolamine	Morpholine
La(NO₃)₃	2.45	7.75	3.74
NdBr₃	0.936	3.20	0.099
NdI₃	2.53	1.93	0.500
Nd(C₂H₃O₂)₃	7.81[a]	18.4	0.175
Y(C₂H₃O₂)₃	6.26[a]	17.6	...

Solubility, g./100 g. of solvent

[a] Solubility in g./100 ml. of solution.

The generally noted increase in solubility in basic solvents on going from anhydrous bromide to anhydrous iodide is borne out by the data for the neodymium compounds, except in monoethanolamine. It is of interest that sodium iodide is also less soluble in monoethanolamine than in ethylenediamine and less soluble than sodium bromide in monoethanolamine.[18] Anomalies of this sort may sometimes be accounted for in terms of solvate formation.

Conductance Studies.—Typical conductance data, as summarized in Tables III–IV, indicate clearly that both ethylenediamine and monoethanolamine are reasonably good electrolytic solvents for the rare earth metal salts studied. Morpholine, on the other hand, is a poor electrolytic solvent, doubtless because of its low dielectric constant.

Lanthanum nitrate and neodymium bromide behave as comparatively strong electrolytes. Although the lack of absolute purity precluded precise measurements with neodymium iodide, such data as were obtained indicated that this compound is an even better electrolyte than neodymium bromide. Neodymium and yttrium acetates, however, behave as weak electrolytes despite their enhanced solubilities. The marked in-

(18) H. S. Isbin and K. A. Kobe, THIS JOURNAL, **67**, 464 (1945).

TABLE III

CONDUCTANCE DATA FOR ETHYLENEDIAMINE AND MONO-
ETHANOLAMINE SOLUTIONS AT 30°

Concn., eq. l.[-1]	La(NO$_3$)$_3$ en[b]	La(NO$_3$)$_3$ ethan[b]	NdBr$_3$ en	NdBr$_3$ ethan	Nd(C$_2$H$_3$O$_2$)$_3$ en	Nd(C$_2$H$_3$O$_2$)$_3$ ethan	Y(C$_2$H$_3$O$_2$)$_3$ en	Y(C$_2$H$_3$O$_2$)$_3$ ethan
0.600							0.200	
.500							.215	3.26
.400							.226	3.50
.300							.241	3.78
.200							.268	4.20
.150		9.5			0.18	4.10	.287	4.51
.100	11.0	10.5			.20	4.59	.335	4.93
.090	12.5	10.6			.21	4.69	.345	5.06
.080	13.5	10.7			.22	4.82	.360	5.17
.070	14.6	11.1			.23	4.93	.376	5.33
.060	15.7	11.4			.25	5.07	.400	5.52
.050	17.0	11.6			.29	5.22	.435	5.72
.040	18.3	11.8			.36	5.50	.475	5.96
.030	21.0	12.1			.46	5.85	.540	6.32
.020	24.9	12.8	17.1	28.0	.62	6.27	.665	7.43
.010	33.0	14.4	21.9	30.7	1.19	7.05		
.009			22.5	31.0				
.008			23.2	31.2				
.007			24.2	31.6				
.006			25.5	31.9			1.70	
.005	42.6	15.7	27.2	32.3	1.92	8.30		
.004			29.0	32.5				
.003			32.0	32.9				
.0025							3.46	
.002	54.5		35.7	34.5				
.001			41.9	38.5				

Equivalent conductance,[a] $\sim$mhos cm.^{2} eq.$^{-1}$

[a] Values interpolated at rounded concentrations. [b] en
= ethylenediamine; ethan = monoethanolamine.

TABLE IV

CONDUCTANCE DATA FOR MORPHOLINE SOLUTIONS AT 30°

Salt	Concn., eq. l.[-1]	Equivalent cond., mho cm.^{2} eq.$^{-1}$
La(NO$_3$)$_3$	0.1156	0.185
NdBr$_3$	.00158	.551
Nd(C$_2$H$_3$O$_2$)$_3$	.0122	.0367

creases in equivalent conductances with increasing dilution are apparent. Plots of the data give smooth curves, that given in Fig. 1 being typical.
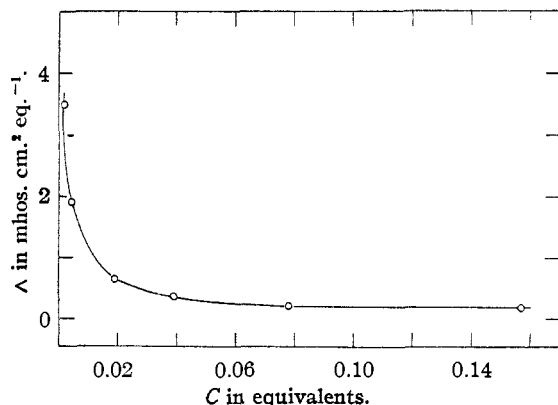

Fig. 1.—Conductivity data for anhydrous solutions of neodymium acetate in ethylenediamine.

Comparisons of data for ethylenediamine and monoethanolamine are of interest. The higher dielectric constant of the latter would imply that it should be the better electrolytic solvent. However, the very high viscosity (Table I) of monoethanolamine reduces ion mobilities markedly and decreases the value of this substance as an ionizing solvent. The interplay of these two factors is reflected in the conductance data. Thus, monoetha-

nolamine is a better electrolytic solvent for acetates, the dielectric constant factor apparently being of the greater importance for these inherently more covalent compounds. On the other hand with stronger electrolytes such as lanthanum nitrate and neodymium bromide, viscosity appears to be the more important factor, the electrolytic solvent properties of ethylenediamine being enhanced accordingly. This is particularly true in dilute solutions where ion mobilities are increasingly important.

The effects of temperature changes upon the conductances of anhydrous ethylenediamine and monoethanolamine and of solutions of yttrium acetate in these solvents are shown in Table V. General increases in conductance with increasing temperature are to be expected because parallel increases in degrees of dissociation and in solvent fluidities are sufficient to overcome any temperature-induced decreases in dielectric constant.

TABLE V

EFFECTS OF TEMPERATURE UPON CONDUCTANCE VALUES

Temp., °C.	Ethylenediamine Solvent × 10^8	Ethylenediamine 0.5909 N Y(C$_2$H$_3$O$_2$)$_3$ × 10^8	Monoethanolamine Solvent × 10^8	Monoethanolamine 0.4758 N Y(C$_2$H$_3$O$_2$)$_3$ × 10^8
10	..	..	1.37	0.76
20	3.53	0.98	1.93	1.12
30	3.88	1.12	2.51	1.61
40	4.32	1.26	3.37	2.24
50	4.57	1.39	4.34	2.89
60	4.84	1.49	5.47	3.66
70	4.94	1.62	6.41	4.43
80	5.04	1.67	..	5.07

Specific Conductance, mho cm.$^{-1}$

It is apparent from the conductance data cited that solutions of at least certain rare earth metal salts in ethylenediamine and monoethanolamine are sufficiently ionic in character to warrant investigation of their behaviors upon electrolysis. It is also apparent, however, that the conductances of these solutions are in general sufficiently small that any successful electrolysis experiments would be complicated by internal resistance effects. In an attempt to improve conductance values, the effects of small additions of water were evaluated for

TABLE VI

EFFECT OF WATER UPON CONDUCTANCE VALUES AT 30°

Water concn., mole l.[-1]	Ethylenediamine × 10^8	0.6509 N Y(C$_2$H$_3$O$_2$)$_3$ × 10^4	Water concn., mole l.[-1]	Ethylenediamine × 10^8	0.6509 N Y(C$_2$H$_3$O$_2$)$_3$ × 10^4
0.0000	3.78	1.42	0.402		3.18
.0456	3.96		.411	8.70	
.0574		1.65	.456	9.34	
.0912	4.76		.460		3.41
.115		2.08	.503	9.92	
.137	5.42		.547	10.4	
.172		2.38	.631		3.99
.228	6.54		.776	11.8	
.230		2.59	.804		4.46
.274	6.99		1.01	13.6	
.287		2.84	1.205		5.33
.320	7.49		1.23	15.5	
.344		3.02	1.492		6.17[a]
.366	8.15				

Specific conductance,

[a] Pptn. at water concentrations above 1.492 M.

ethylenediamine and for a solution of yttrium acetate in this solvent. Although large quantities of water cause precipitation in this and other comparable systems, as previously noted, reasonable quantities of water can be added. As indicated by the data summarized in Table VI, the presence of water short of precipitation does increase conductance values. Comparison of the values for the pure solvent with those for the solution suggests that improved conductance in the latter cannot be

due to increase in solvent conductance alone. It seems probable that another factor is the replacement of ethylenediamine molecules by water molecules in the solvated cation to give smaller, more mobile species. Comparable observations were made with other rare earth metal salts.

URBANA, ILLINOIS

Quantity Separation of Rare Earths by Liquid–Liquid Extraction. I. The First Kilogram of Gadolinium Oxide[1]

BY BOYD WEAVER, F. A. KAPPELMANN AND A. C. TOPP

Countercurrent liquid–liquid extraction techniques have been successfully applied to the separation of large quantities of rare earths—specifically for the purification of gadolinium. The solvents used were *n*-tributyl phosphate and nitric acid. More than a kilogram of better than 95% gadolinium oxide has been produced. Increases in temperature have been found to decrease extraction into the organic phase. Distribution coefficients of rare earths between freshly prepared tributyl phosphate and nitric acid are nearly independent of rare earth concentration within the practical operating range.

Introduction

Liquid–liquid extraction is theoretically the most promising method of separating rare earths. The chief requirements are that there be adequate differences in distribution factors between successive elements and that it be possible to maintain these differences throughout a multistage countercurrent extraction system. Many investigations have been conducted in this field. Most of them have remained unpublished because separation factors were too small or individual distribution coefficients were too small or too large. Appleton and Selwood[2] expressed interest in developing a process for which the separation factor between neodymium and lanthanum was only 1.06. Templeton and Peterson[3] obtained a factor of 1.5 between these elements by extraction with hexanol from nitrate solutions, but individual extraction coefficients were small. The claims of Fischer, Dietz and Jübermann[4] in 1937 that numerous combinations of salts and solvents gave separation factors of 1.5 between adjacent elements do not agree with the experience of other workers and these authors have never given any concrete evidence of such success. A 1950 review by Bock,[5] of Fischer's laboratory, dismisses extraction methods with pessimism.

The observations of Peppard,[6] *et al.*, were far more promising. They reported that by the use of

tributyl phosphate and 12 *N* nitric acid, separation factors of about 2 between adjacent elements were attained, and distribution coefficients were satisfactory for operation of standard extraction equipment. While their work was all done on a tracer or small batch level and included only a few of the rare earths, it was evident that the process could be applied to a continuous countercurrent system for the separation of all of these elements.

The present authors had need of kilogram quantities of each of several of the elements with high purity for use in the electromagnetic separation of their isotopes. Only lanthanum, cerium, neodymium and samarium were readily available in sufficient quantities. The expense and labor necessary to produce the others by conventional methods were prohibitive. Therefore, development of the extraction process was undertaken to supply these needs. Special attention was given first to gadolinium, the most abundant of the remaining elements. The separation was approached as a production problem, with investigation of details of extraction characteristics being limited to the solution of specific problems encountered as the work progressed.

Experimental

Batch Countercurrent Fractionation.—A pseudo-countercurrent batch system was set up consisting only of beakers with drains and motor driven stirrers. The organic solvent was always a 60:40 mixture of tributyl phosphate and Varsol,[7] equilibrated with concentrated nitric acid. With other conditions fixed, the point at which a mixture of rare earths is divided is dependent only upon the ratio of the volumes of organic and aqueous solvents used. Purification of a single element requires separation first on one side of it, then on the other.

The first aim was to split the mixture between samarium

(1) Presented before the Division of Physical and Inorganic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, September, 1952.

(2) D. B. Appleton and P. W. Selwood, THIS JOURNAL, **63**, 2029 (1941).

(3) C. C. Templeton and J. A. Peterson, *ibid.*, **70**, 3967 (1948).

(4) W. Fischer, W. Dietz and O. Jübermann, *Naturwissenschaften*, **25**, 348 (1937).

(5) R. Bock, *Angew. Chem.*, **62A**, 375 (1950).

(6) D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, **57**, 294 (1953).

(7) Varsol is the trade name of a petroleum fraction similar to kerosene but purified from gasoline. It does contain unsaturated hydrocarbons.